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THE INFLUENCE OF MONOMER CHEMICAL STRUCTURE ON LATE-STAGE CURE KINETICS OF DICYANATE ESTER RESINS

20 October 2011

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Outline

- Background: Unusual Structure-Property Relationships in High-T_g Thermosetting Polymers
- Results:
  - Comparison of late stage cure kinetics for three dicyanate monomers
  - Role of flexible network junctions
  - Effect of cure on moisture uptake
- Implications for Composite Resin Development

Acknowledgements: Air Force Office of Scientific Research, Air Force Research Laboratory

Propulsion Research at AFRL

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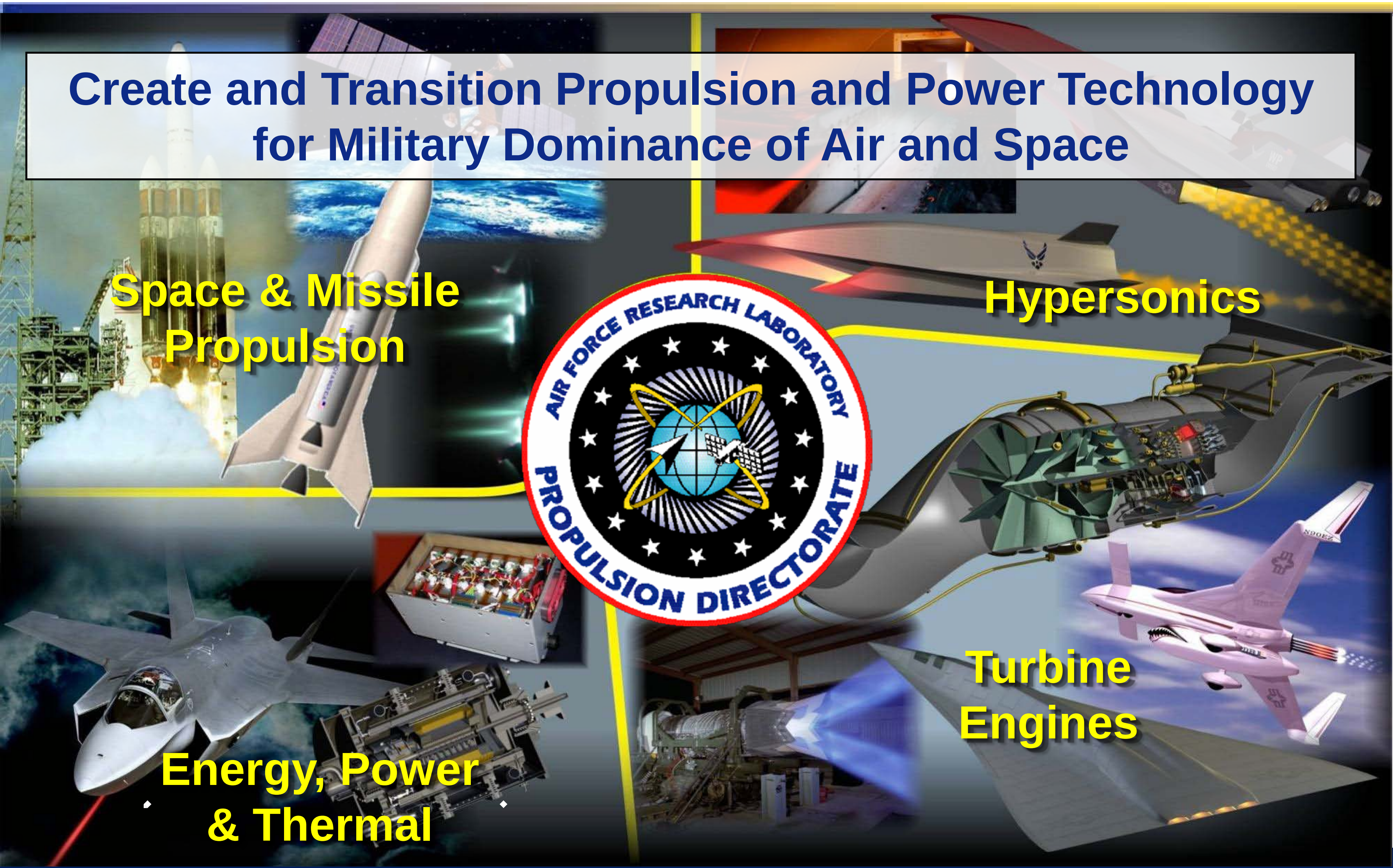
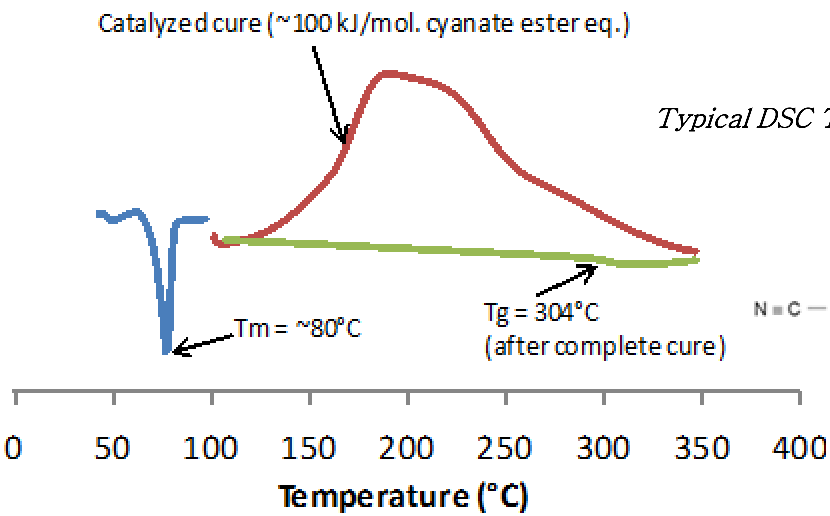
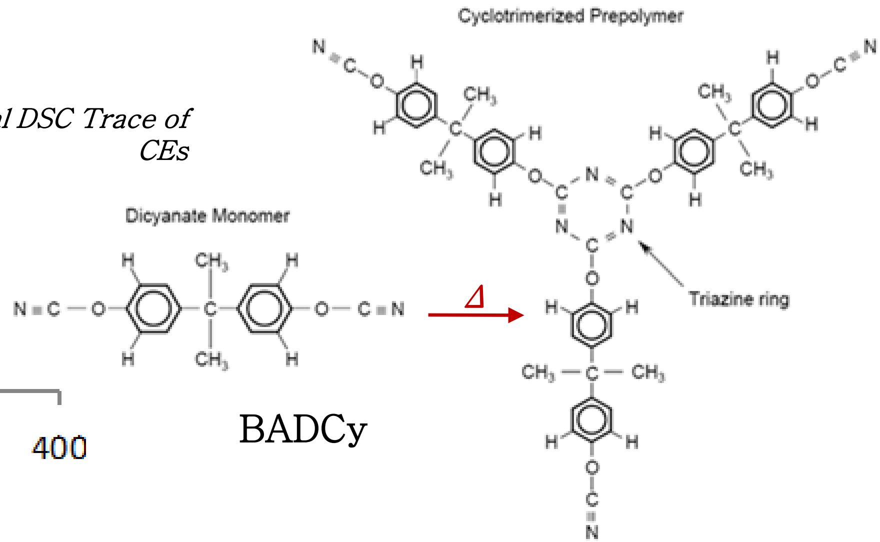


Model High-Temperature Thermosetting Polymers: Cyanate Esters



Typical DSC Trace of CEs



- Glass transition temperatures at full cure of 200 – 400°C
- Uncured resins exist as low-melting solids, or low to moderate viscosity liquids, making them ideal for processes such as filament winding
- Broad compatibility with co-monomers, thermoplastic tougheners, or nanoparticles for control of physical and mechanical characteristics
- Single species reaction chemistry is “cleaner” than epoxy resin and well-understood; enables development of superior predictive models for failure; readily catalyzed to cure at reasonable temperatures

Cyanate Esters: Universe of Applications

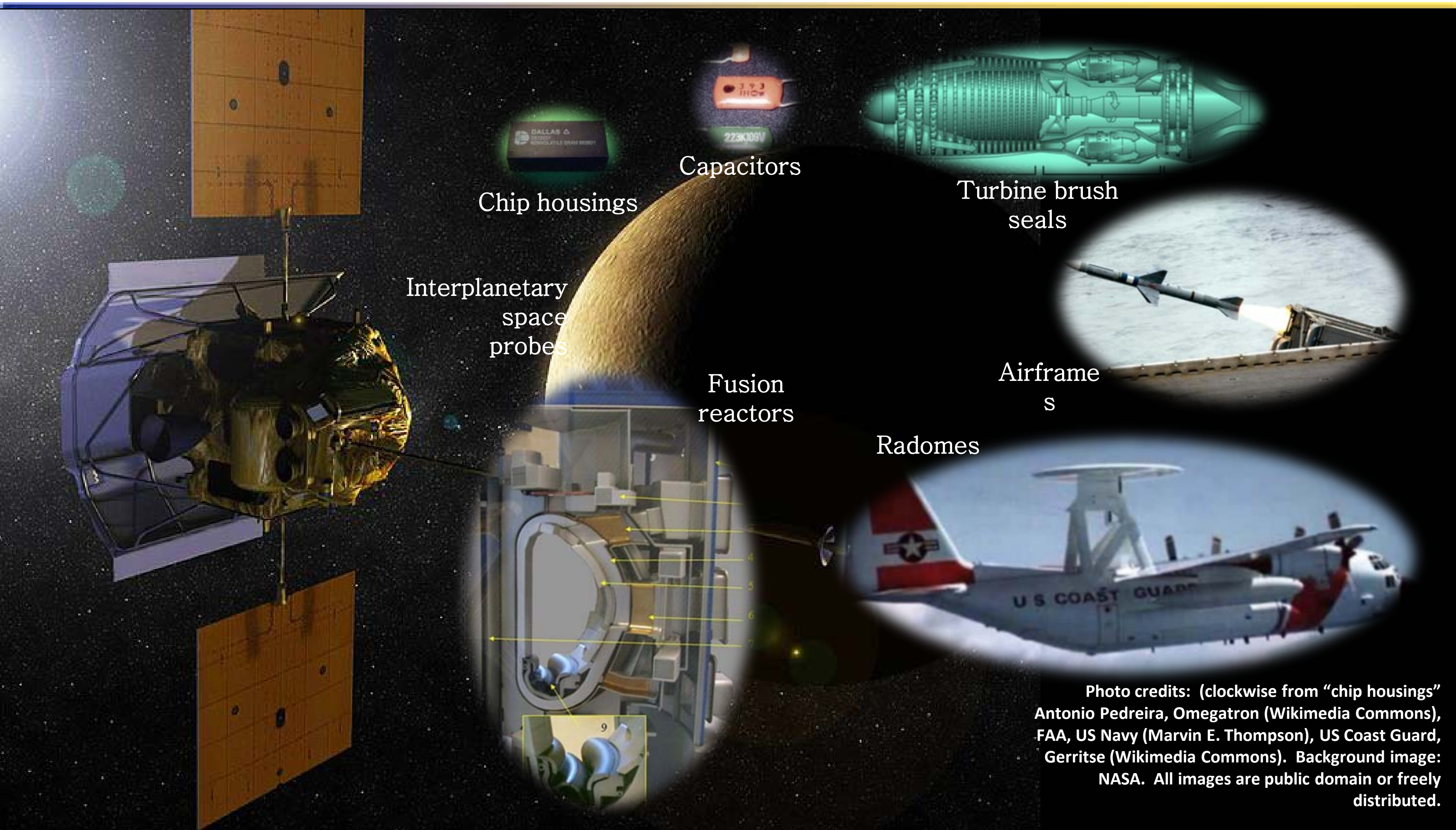


Photo credits: (clockwise from "chip housings" Antonio Pedreira, Omegatron (Wikimedia Commons), FAA, US Navy (Marvin E. Thompson), US Coast Guard, Gerritse (Wikimedia Commons). Background image: NASA. All images are public domain or freely distributed.

- Many opportunities for technical transition …

Examples of Cyanate Ester Resins

Name	T_{g0}(°C)*	$T_{g\infty}$ (°C)*	Density* (g/ccl)	Water Uptake*
BADCy	-38	304	1.195	2.3%
LECy	-47	290	1.220	2.4%
SiMCy	-46	260	1.175	1.8%

***after full cure w/ primary cure at 210 °C, systems include catalyst with 160 ppm Cu(II) as Cu(II)AcAc with 2 phr nonylphenol**

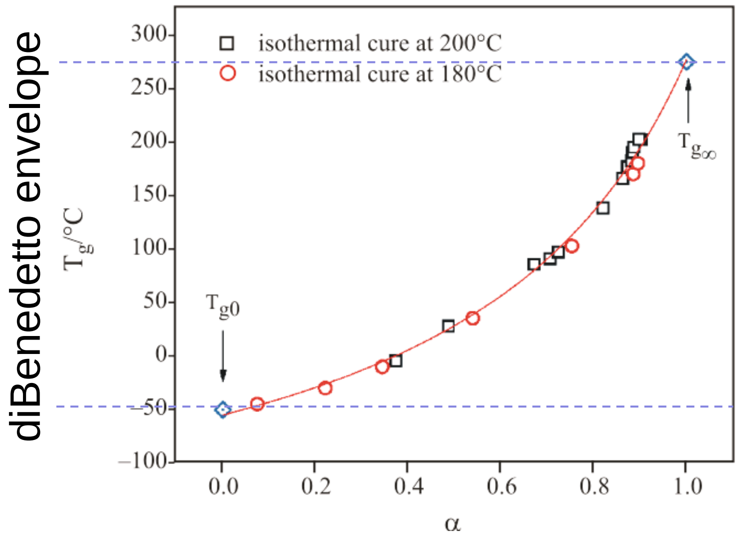
"BADCy"

"LECy"

"SiMCy"

- BADCy was the first-commercialized cyanate ester; it is least expensive and has the largest property database
- LECy is the most common room-temperature liquid dicyanate ester often used in filament winding formulations
- SiMCy is a highly useful BADCy analog first synthesized by Wright *et al.* (*Polym. Prepr.* **2004**, *45* (2), 294) noted for its low water uptake

Glass Transition as a Function of Extent of Cure in a Thermosetting Polymer

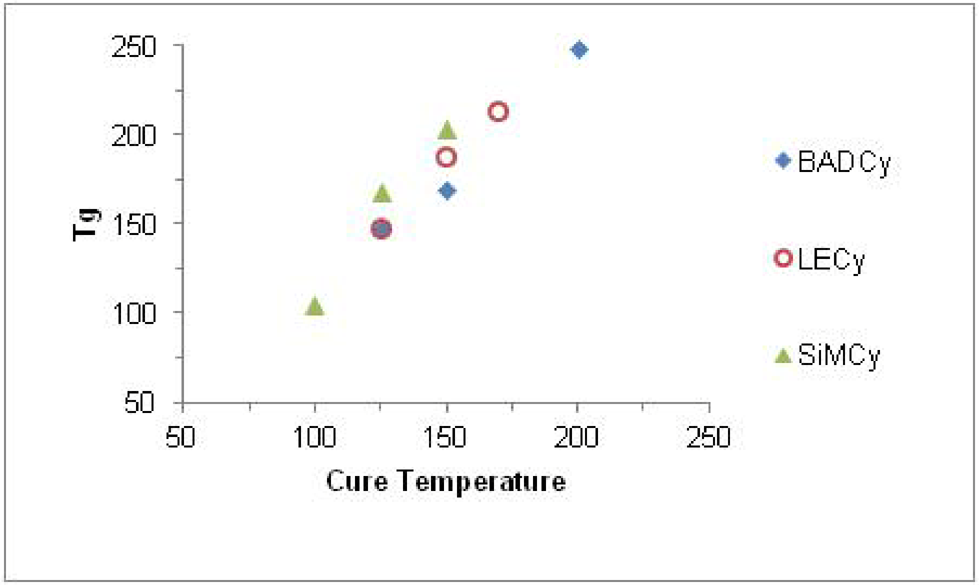


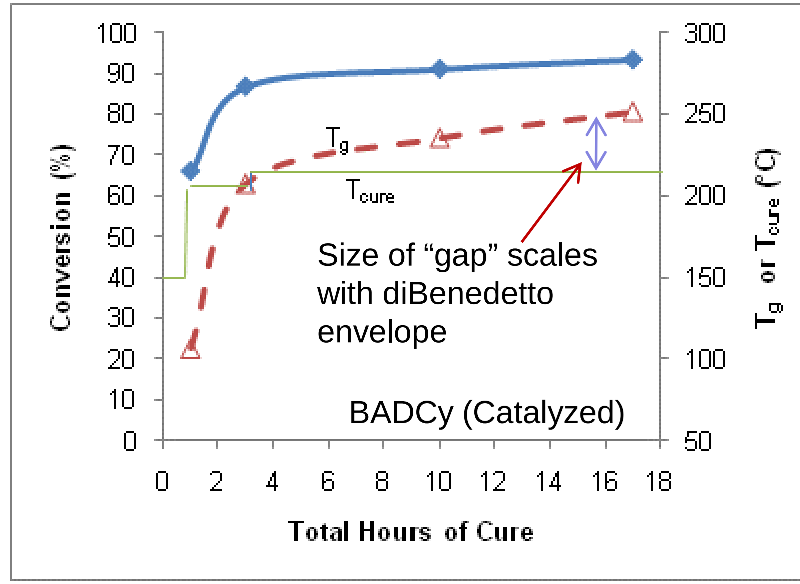
An example of how T_g values can be converted to conversion values based on the diBenedetto equation (from X. Sheng, M. Akinc, and M. R. Kessler, *J. Therm. Anal. Calorim.* **2008**, 93, 77-85.) for EX-1510 dicyanate ester resin, for which $T_g << T_{decomp}$

- Note the steep dependence of T_g on conversion as the system reaches full cure
- The need for higher use temperatures pushes up $T_{g\infty}$ as better performing resins are developed
- The need for ease of processing dictates that T_{g0} remain low, preferably below room temperature
- As a result, composite resins are evolving to have an ever steeper diBenedetto curve, which results in a very strong dependence of T_g on conversion.
- Normally, T_g depends on free volume in polymers, but as conversion dependence begins to dominate, the rules for structure-property relationships change

Material °C→	T_{g0}	$T_{g\infty}$	ΔT_g	$dTg/d\alpha\|_{\alpha=1}$
Epoxy	0	150	150	4.5
Polyimide	200	450	250	7.5
Cyanate Ester	-50	300	350	10.5

A Large diBenedetto Envelope Means T_g Exceeds T_{cure} at Late Stages of Cure





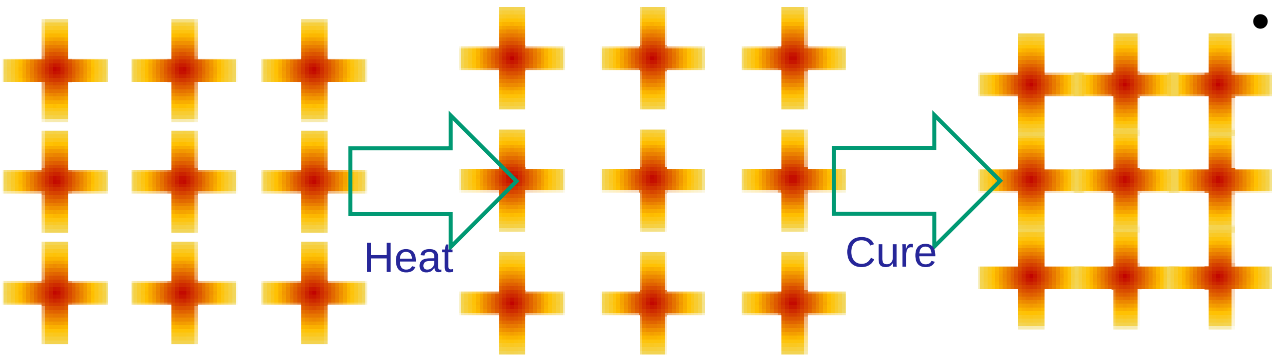
T_g (°C) of Cyanate Esters Cured 12 h

T_{-Cure} (°C)	125	150	170	200
BADCy	134	168	--	246
LECy	142	183	213	--
SiMCy	152	186	--	--

- Vitrification slows down conversion, but does not stop it completely
- Under isothermal conditions, the rate of conversion will fall as conversion increases, but the sensitivity of T_g to conversion will rise, resulting in a fairly constant rise in T_g
- The greater the sensitivity, the further T_g can rise above T_{cure}

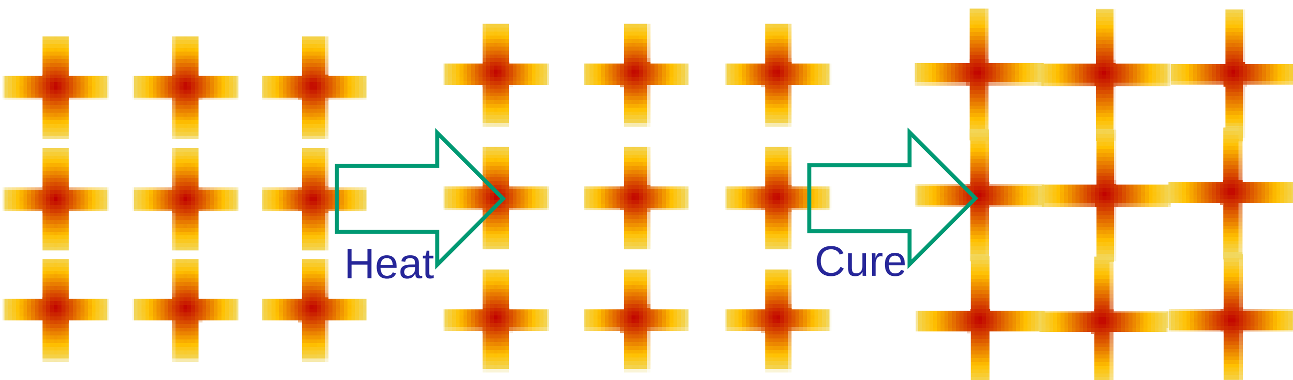
“Vitreous Cure” Differs Markedly from Main Stage Cure

Main Stage Thermal Cure



- Cure results in:
  - *Net Shrinkage*
  - *Less permeability*
  - *Higher modulus*
  - *Brittleness*

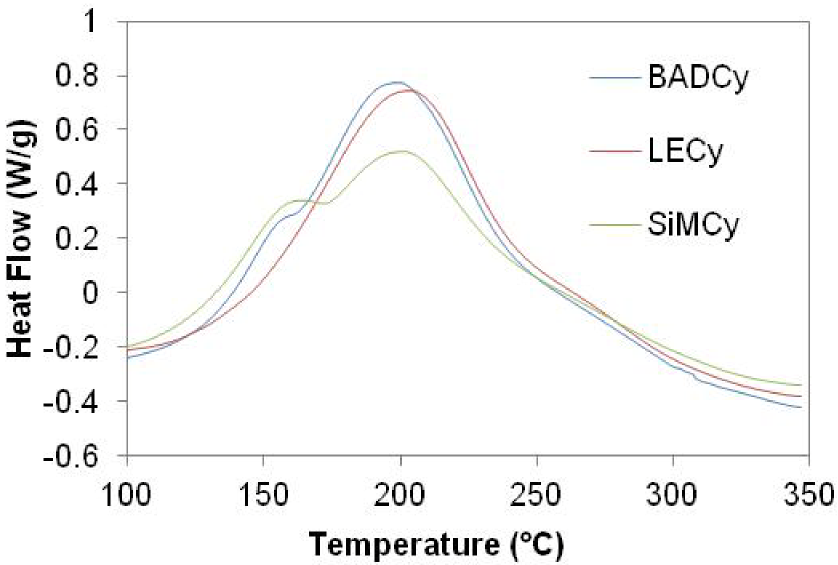
“Vitreous Cure”

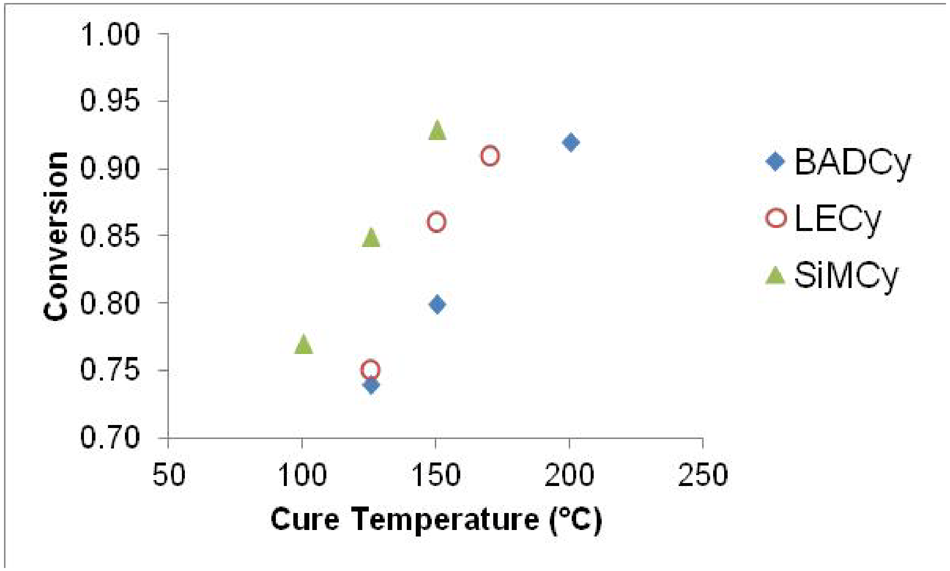


- Cure results in:
  - *Net Expansion*
  - *Higher permeability*
  - *Lower modulus*
  - *Toughness*

- “Vitreous Cure” is promoted by rigid network segments with well-distributed extensibility, and by cure temperatures that are low in comparison to T_g (though $T_{cure} < T_g$ may not be a criterion)
- Both types of cure can happen sequentially, simultaneously, or in mixed form

Comparison of Dicyanate Resins in Main Stage and Late Stage Cure Kinetics



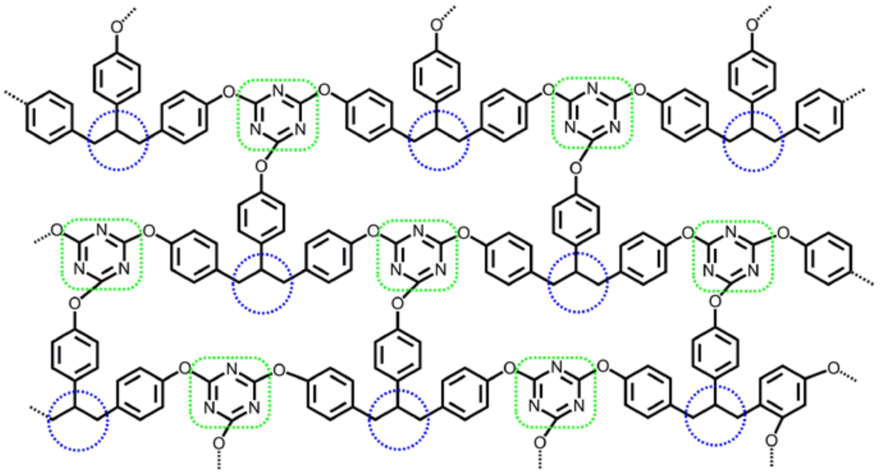


- The DSC curves (main stage cure) show reactivity increases in the order LECy < BADCy < SiMCy, with the shape of the curves indicating catalysis is primarily responsible for the differences (peak heat release temperatures are nearly identical).
- In contrast, in late stage cure, the reactivity increases in the order BADCy < LECy < SiMCy, with both the overall conversion and the effectiveness of increased temperature in achieving marginal conversion following the same trend, suggesting that molecular structure, most likely bond flexibility, controls the reactivity.

The Role of Flexible Junctions in Cyanate Ester Networks

GOAL: Replace cyanurate linkages with alternative network linkages to generate high Tg values via a high density of cross-linked network junctions without increasing water uptake, and while preserving toughness.

"FlexCy"



AF/Navy Collaboration:

Monomer synthesized by Dr. Matthew Davis at NAWCWD China Lake

NAVAIR

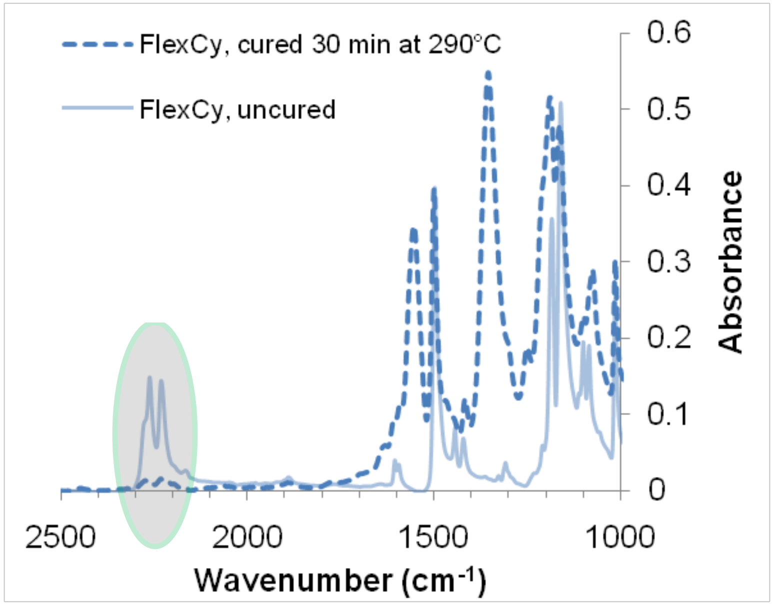
Publications:

Guenthner, A. J.; Davis, M. C.; Lamison, K. R.; Yandek, G. R.; Cambrea, L. R.; Groshens, T. J.; Baldwin, L. C.; Mabry, J. M. "Synthesis, Cure Kinetics, and Physical Properties of a New Tricyanate Ester with Enhanced Molecular Flexibility", *Polymer*, 2011, 52, 3933-3942

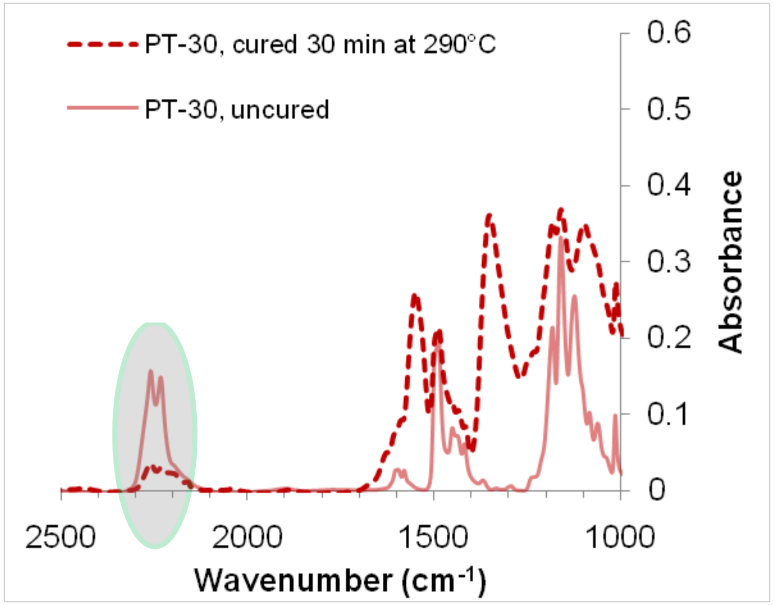
; see also, same authors, "Cure Characteristics of Tricyanate Ester High-Temperature Composite Resins" in *Proceedings of SAMPE '11*.

Flexible Junctions Promote Late Stage Cure in Tricyanates as Well as in Dicyanates

FlexCy



PT-30



- FT-IR conversion estimates of 95% (FlexCy) and 80% (PT-30) are only approximate but show clearly that incorporation of the alternative linkage types facilitates full cure of the cyanate ester groups, improving dry T_g and toughness.
- Because of the high sensitivity of T_g to conversion that results from the large diBenedetto envelope, the T_g increase driven by higher conversion can outweigh the expected T_g decrease due to incorporation of flexible chemical bonds.

Effect of Vitreous Cure on Physical Properties

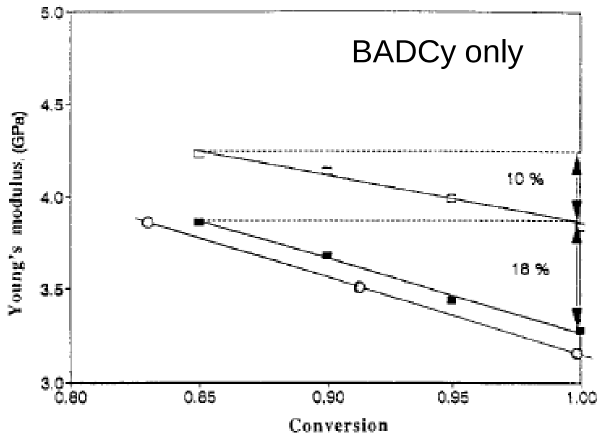
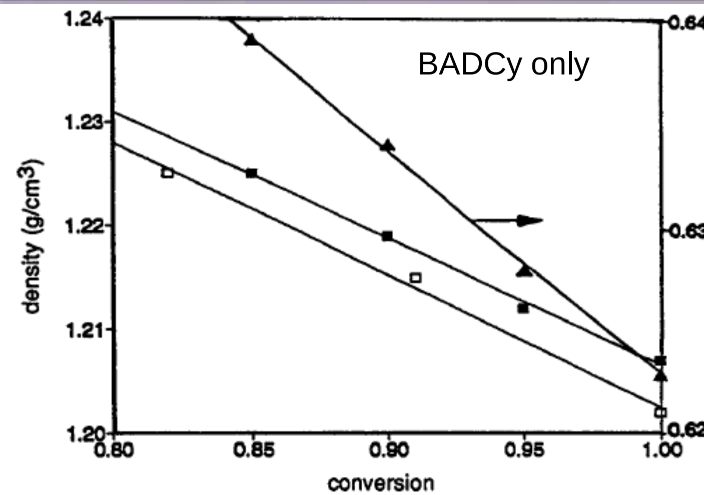


Figure 2 Variation of the (■) Young's modulus and (□) ultrasonic modulus as a function of conversion (uncatalyzed networks). (○) Variation of the Young's modulus of catalyzed networks.

Georjon O and Galy J. *Journal of Applied Polymer Science 1997;65(12):2471-2479.*

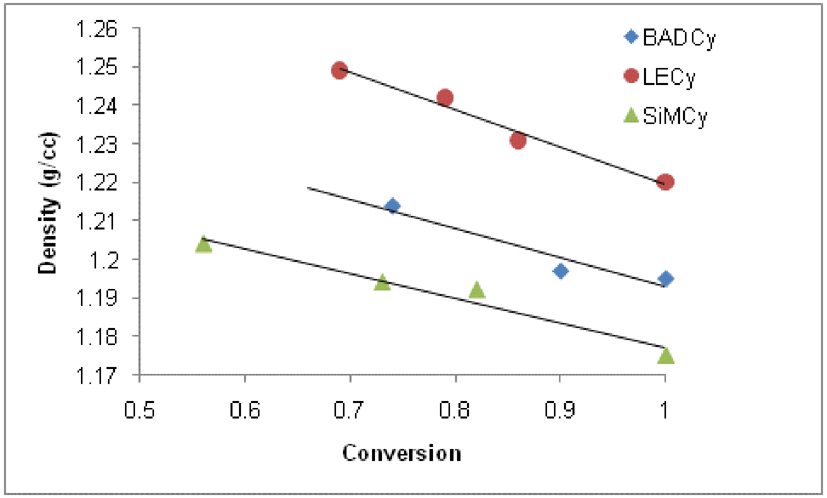


Georjon, O. and Galy, J. *Polymer* 1998, 39, 343

Figure 3 Density values as a function of conversion (at room temperature): ■, uncatalysed networks; □, catalyzed networks; ▲, packing density of uncatalysed networks

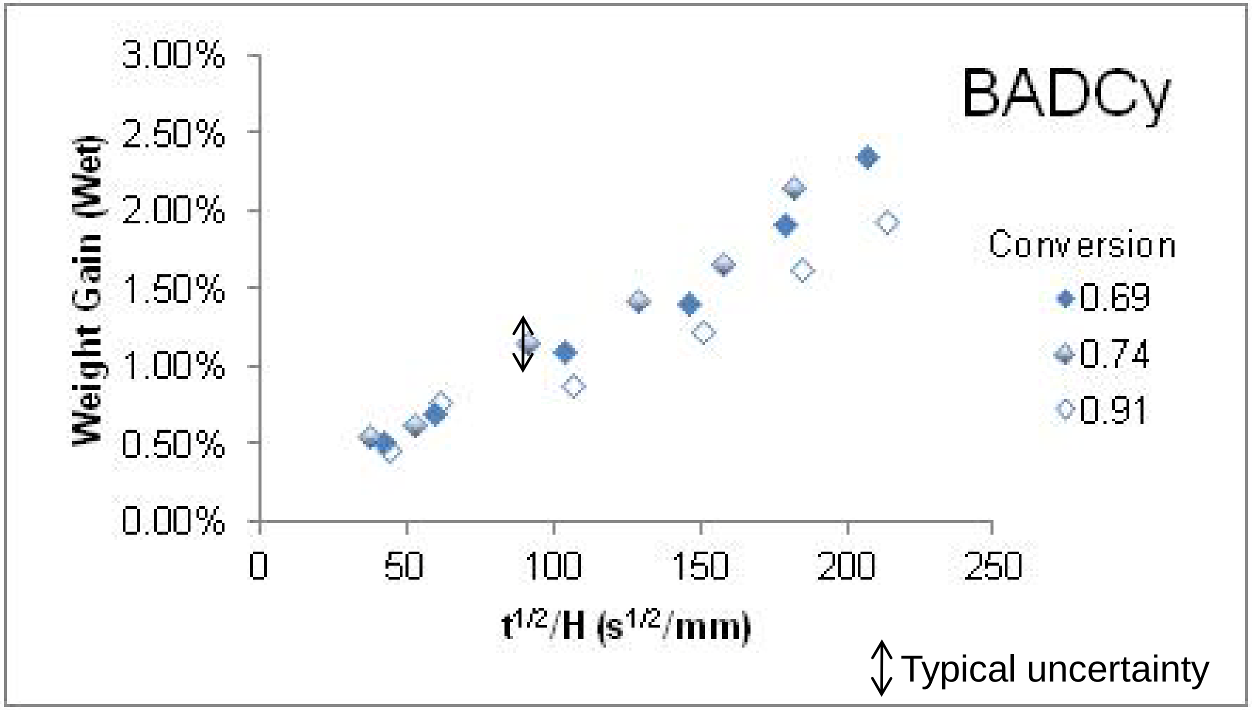
Table V Values of Stress Intensity Factor K_{IC} and Fracture Toughness G_{IC} for Different Polycyanurate Networks BADCy only

Network	K_{IC} (MPa $\sqrt{m}$)	G_{IC} (J/m^2)
100	0.8	170
95	0.5	60
90	0.5	55
85	0.3	20
C100	0.9	220
C91	0.6	90
C82	0.4	35



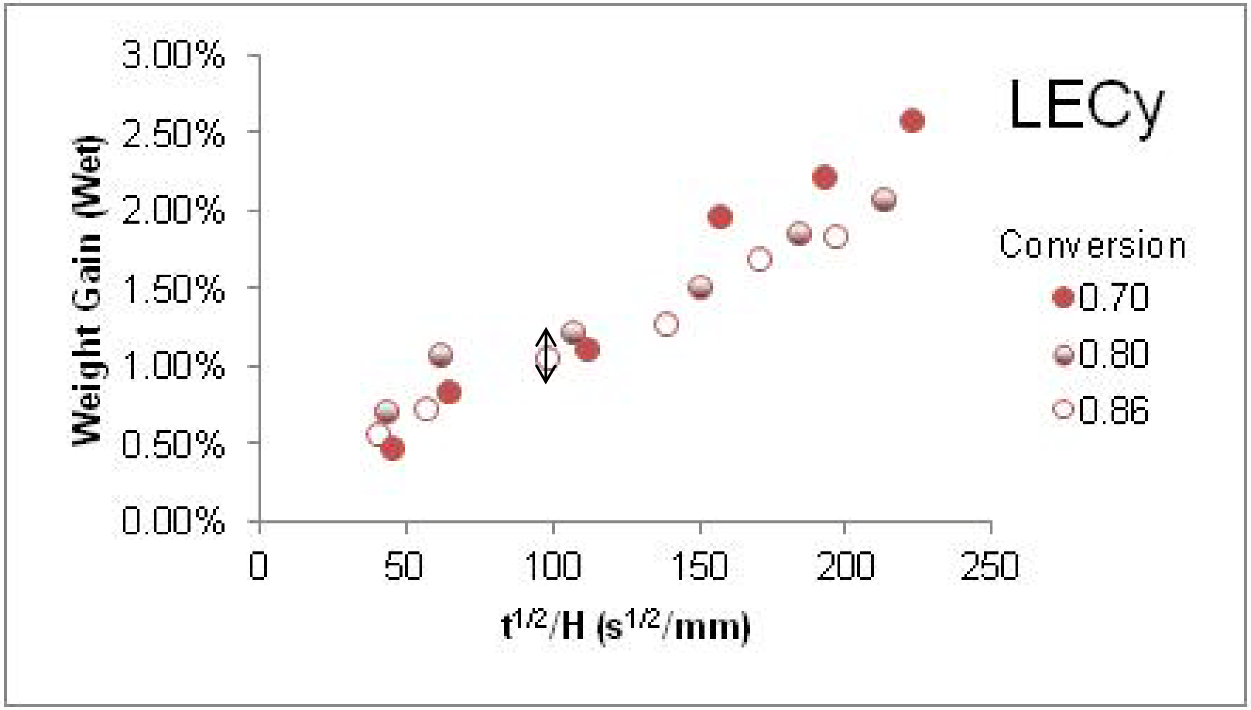
… as confirmed by recent AFRL data

Water Uptake of BADCy as a Function of Conversion



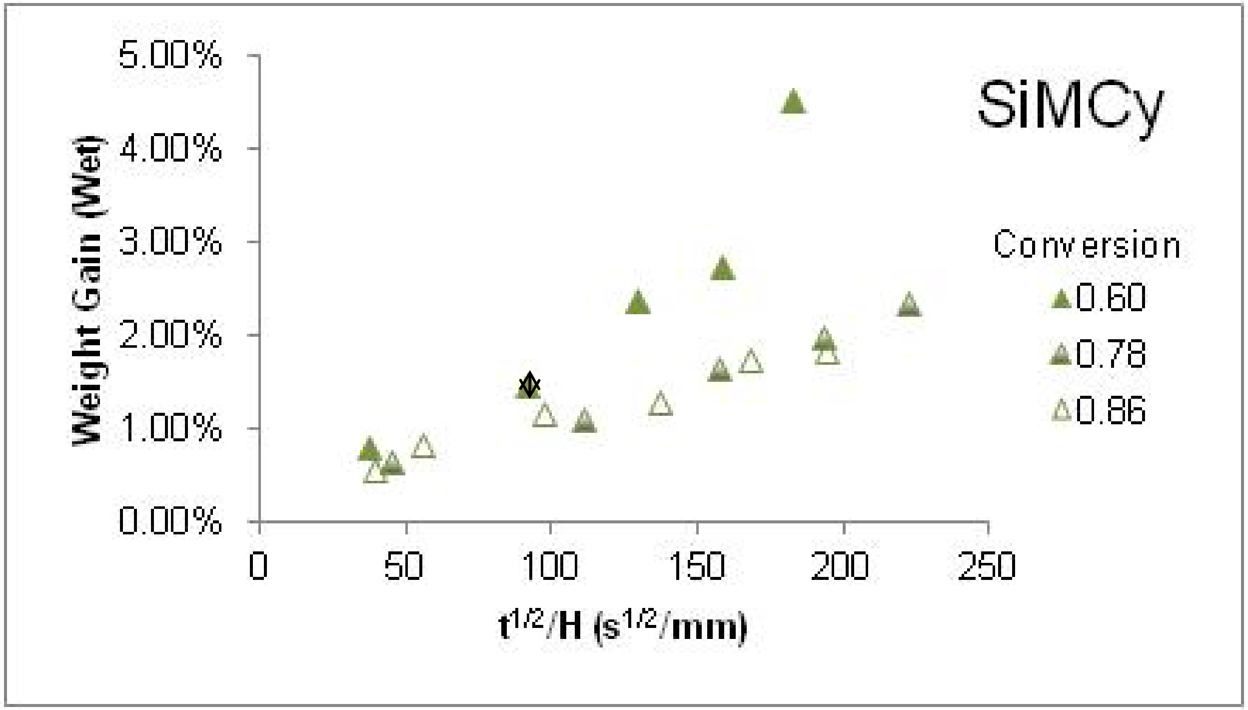
- Scaling of the data to the square root of time and to thickness is meant to produce a linear curve at early times.
- Overall, there is a decreasing level of moisture uptake with increasing conversion, though previously published data shows that at conversions above 90%, water uptake begins to increase with increasing conversion.

Water Uptake of LECy as a Function of Conversion



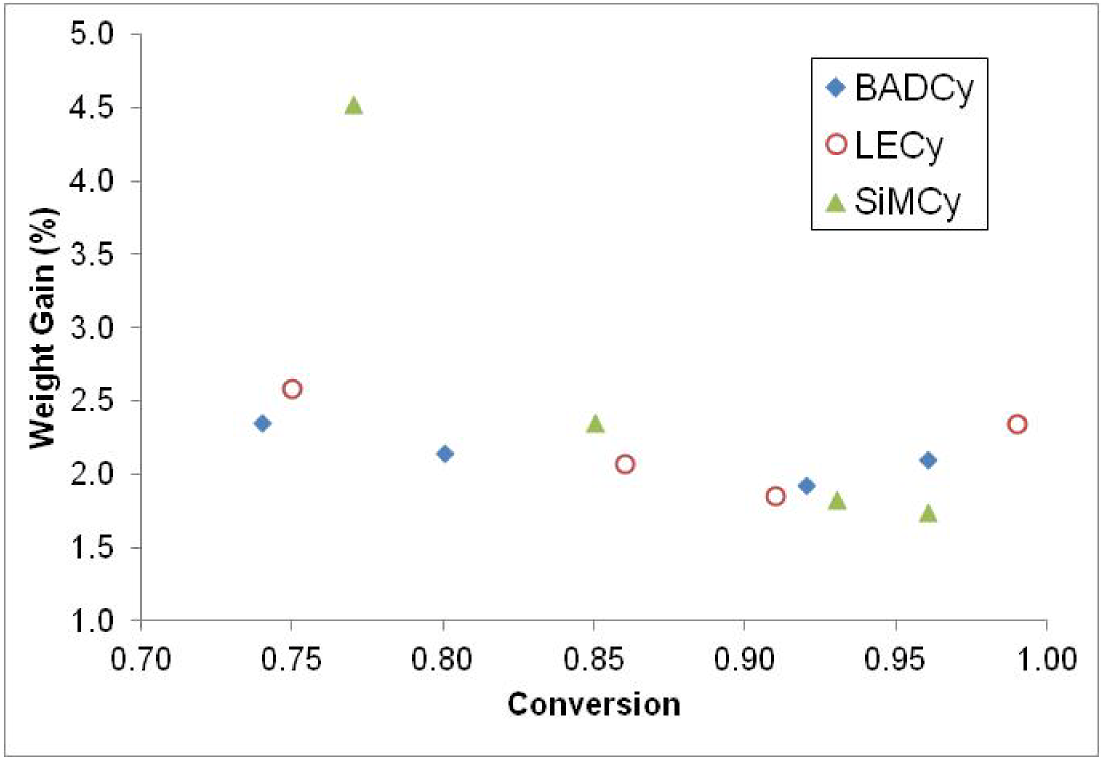
- The trend for LECy is similar to BADCy; increasing conversion leads to decreased water uptake

Water Uptake of SiMCy as a Function of Conversion



- The water uptake data for SiMCy shows significantly higher dependence on conversion. At conversions of 0.6, the upward curving data indicates that water uptake was accelerated by factors other than diffusion, most likely network degradation leading to a glass transition temperature near to or below the exposure temperature.

Water Uptake at 96 hrs as a Function of Conversion in Dicyanates



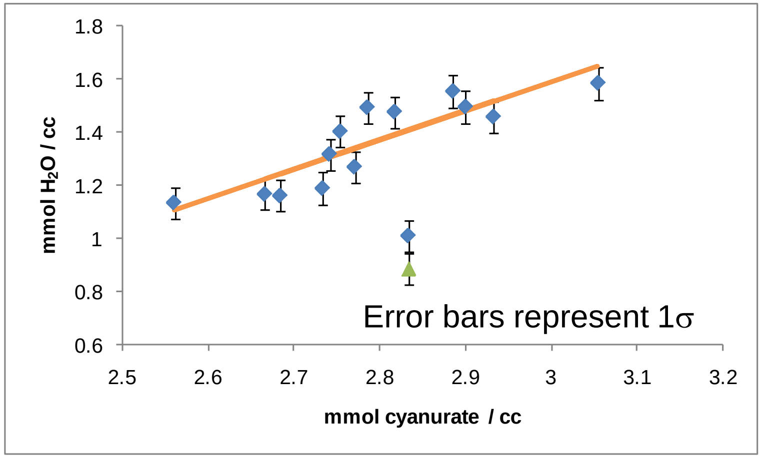
- A comparison of water uptake data for the three monomers (including data from an earlier blend study) shows minima for BADCy, and LECy at around 90%. Blend data also indicate indirectly that the minimum for SiMCy is more likely to be at around 95%, rather than 100%, conversion.

Correlation Between Water Uptake, and Cyanurate Density

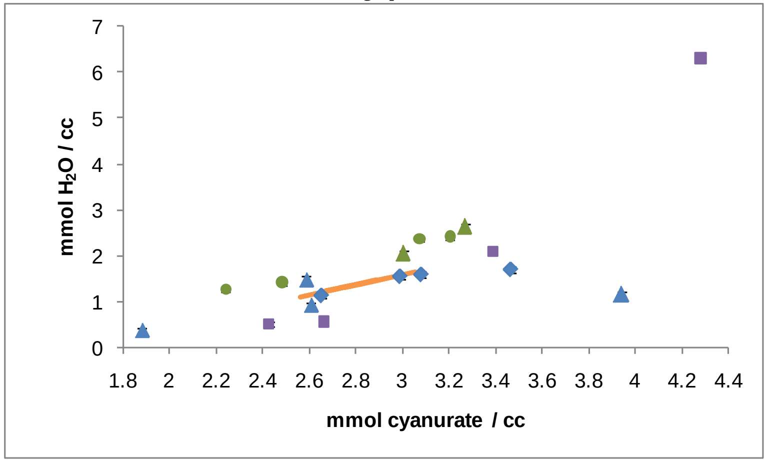
Cyanate Ester - mmol cyanurate/ cc	mmol H_2O / cc
BADCY /3.0	1.7
LECY/ 3.0	1.6
SIMCY / 2.7	1.1
THIOCY / 3.9	1.2
METHYLCY / 2.6	0.9
AroCy F / 2.6	1.5
REX-371 / 3.3	2.6
RTX366 / 1.9	0.4

•Based on data in Appendix a-3 of Hamerton, I (ed)., Chemistry and Technology of Cyanate Ester Resins (Blackie Academic, 1994) (uses monomer density)

In blend samples studied …



… and over all types of CE resins …

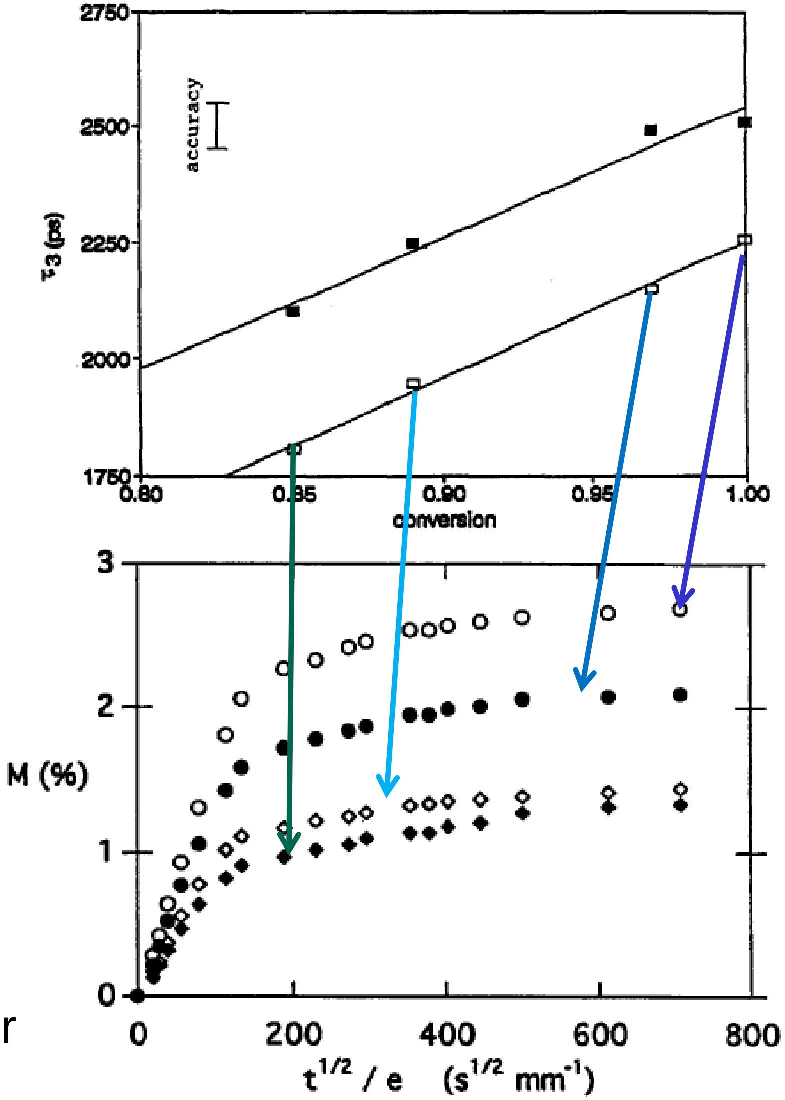


Blue = bisphenyl
Green = three-arm
Purple = single-ring (meta)
Orange = blend data
Triangle = lit. value (x-axis uncertain)

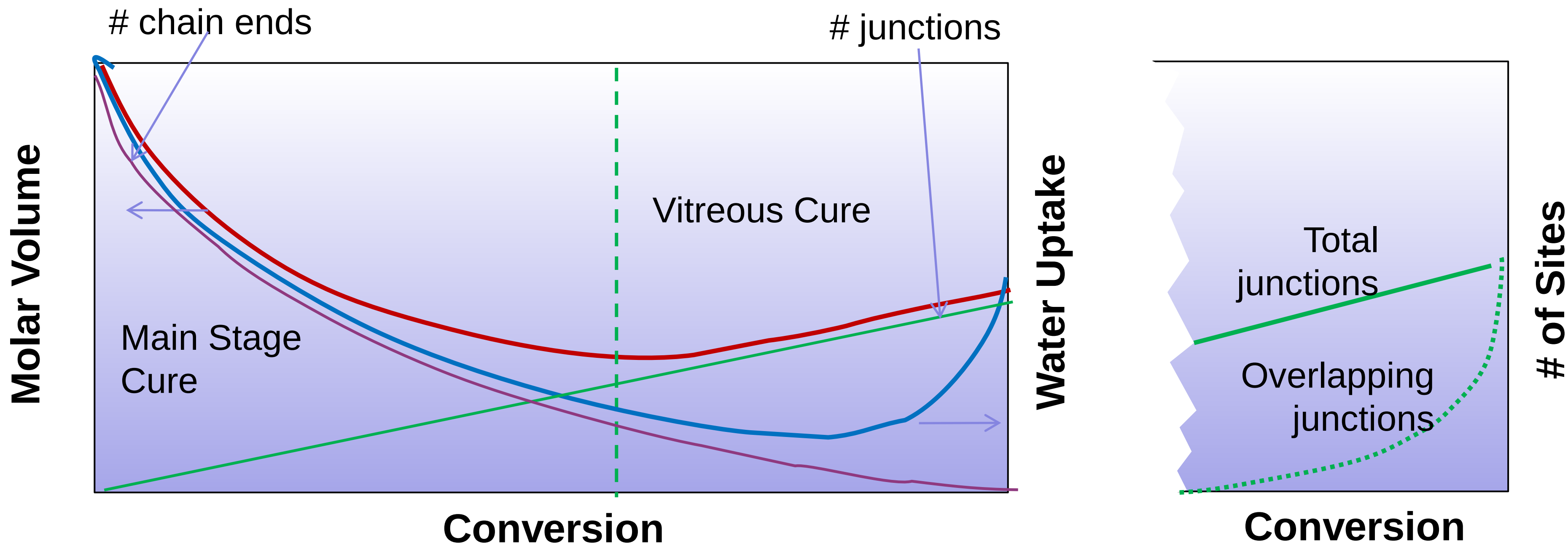
- Maintaining a low density of cyanurate groups appears to limit water uptake

Water Uptake and Free Volume Associated with Cyanurate Groups

- Georjon and Galy (Polymer 39, 343, 1998) showed that, for BADCy, the late stages of cure led to an increase in free volume associated with the formation of cyanurate groups, and that the formation of free volume was directly connected to increased water uptake.
- Our results to date show:
  - A similar correlation at high conversion for other dicyanate monomers
  - That the effect is limited to very high conversions (at lower conversions, free volume increases but water uptake decreases)
  - Monomers with more free volume overall tend to absorb less water
- Thus, all free volume is not equally useful for water uptake.



Possible Explanations for the Effect of Conversion on Water Uptake

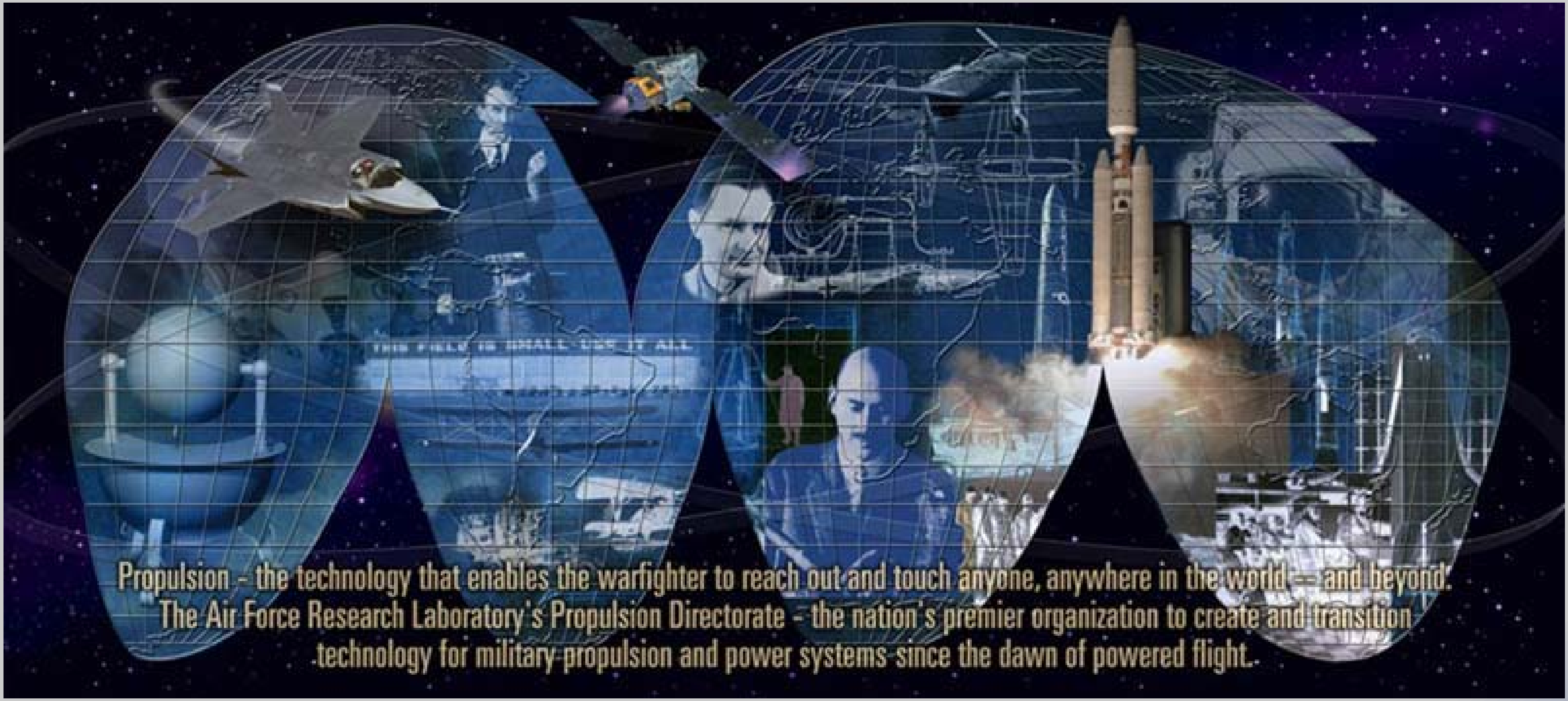


- Water has a greater affinity for chain ends than junctions due to relaxation (does not explain differences among monomers).
- Free volume in proximity to multiple junctions is required to create a favorable site for water uptake
  - Explains steepness of uptake as a function of cross-link density
  - Explains very low uptake in some cyanate ester resins (e.g. RTX-366)
- Effect of co-varying cure temperature and conversion is also beingg checked

Implications for Composite Resin Development

- Awareness of the Unusual Structure-Property Relationships Helps to …
  - Minimize moisture uptake and improve hot / wet performance in high temperature polymer matrix composites
  - Take advantage of previously unrecognized means of improving resin toughness (near-complete cure and judicious use of flexible bonds) without sacrificing high use temperatures
  - Better understand the impact of cure schedule on physical properties
- Impact for USAF: More Reliable and Better-Performing Rocket / Airframe Propulsion
  - Hot / wet performance is often the limiting performance factor
  - Detection of mechanical damage is the major reliability concern

Atlas V



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